NMR relaxometry to monitor *in situ* the loading of an ion exchange resin with Ni^{2+} ions during a column experiment

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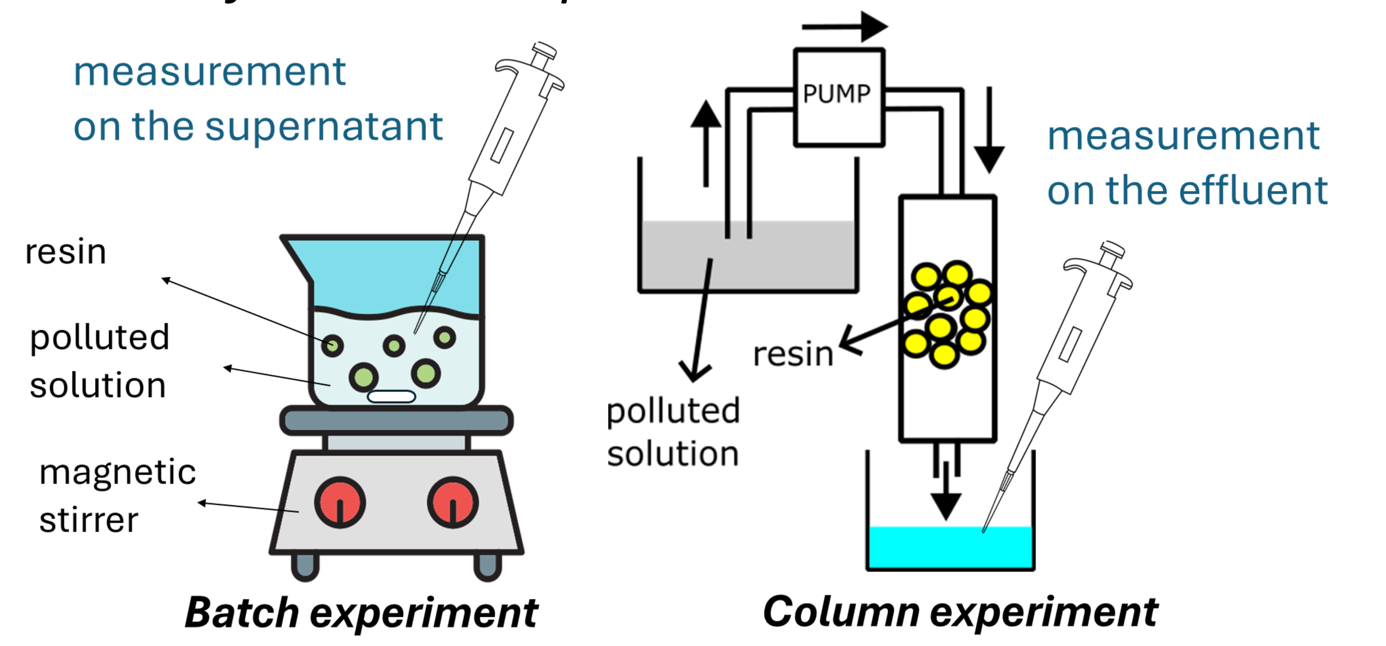
The T_2 relaxation curves of water are used to follow, during a column experiment and directly on the resin bed, the gradual loading of an ion exchange resin with Ni^{2+}. The column is directly inserted into the bore a low-field benchtop NMR device.

1. Water pollution by Nickel

- Nickel found in different industrial wastewaters (metal mining, nickel plating…),
- Its concentration in drinking water should be below 0.07 mg/ml (1.2 µM),
- Ion exchange resins are often used to remove Ni^{2+} from water.



2. Batch and column experiments

- To evaluate the efficiency of a resin: batch or column experiments,
- Batch = simply shaking the metal containing solution with the resin + measurement of $[Ni^{2+}]$ in the supernatant,
- Column = real filtration experiment, the solution flows through the resin bed + measurement of $[Ni^{2+}]$ in the effluent.

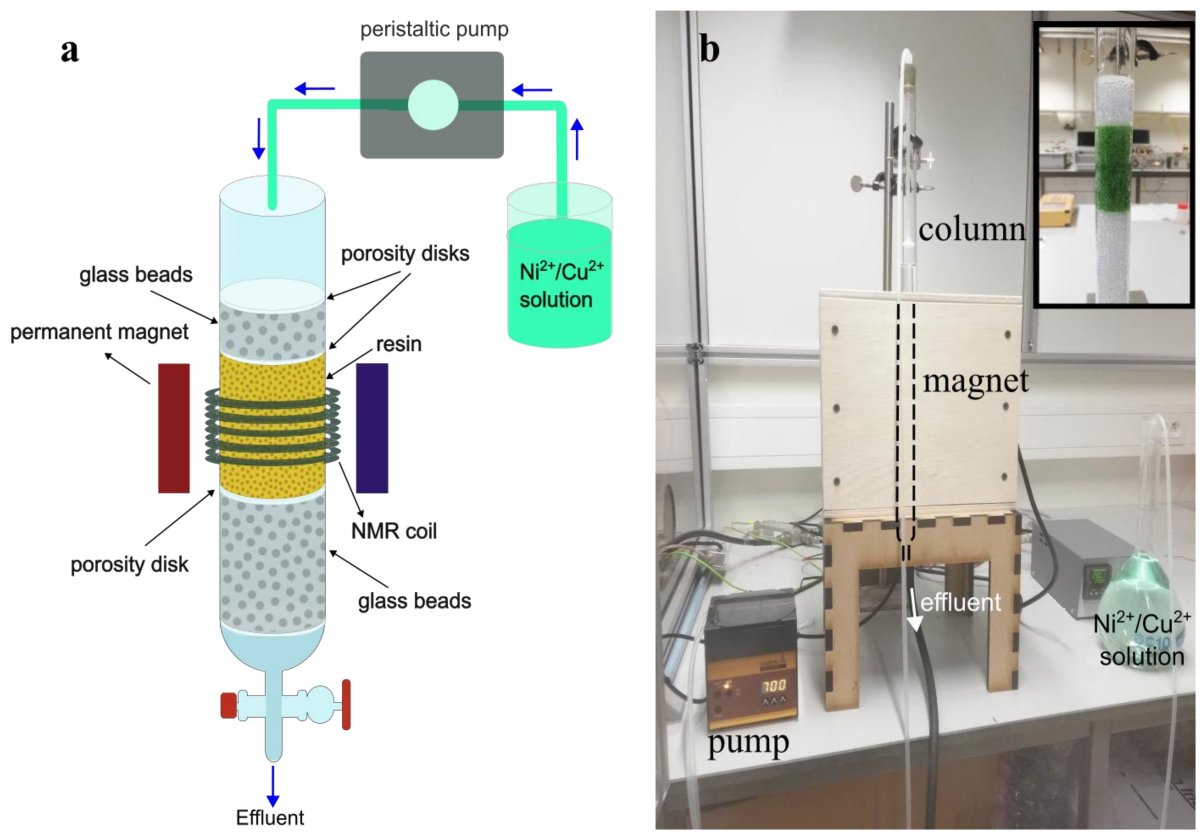


Figure 1: (a) Sketch of the experimental setup. (b) Picture of the actual experiment. The inset shows a close-up of the column after saturation with Ni^{2+}.

3. Why NMR relaxometry to study Ni^{2+} removal by an ion exchange resin?

- Ni^{2+} is paramagnetic => effect on water relaxation, T_1 and T_2 ↘↘ ($r_2 \approx 0.65$ s^{-1}mM^{-1} at 10 MHz)
- Already used to follow Cr^{3+}, Cu^{2+} and Ni^{2+} removal by NMR relaxometry in batch experiments[1-3],
- Relaxation of water present in the intraporosity of the Ni^{2+}-loaded resin also much faster.

4. Setup of a column experiment monitored by NMR

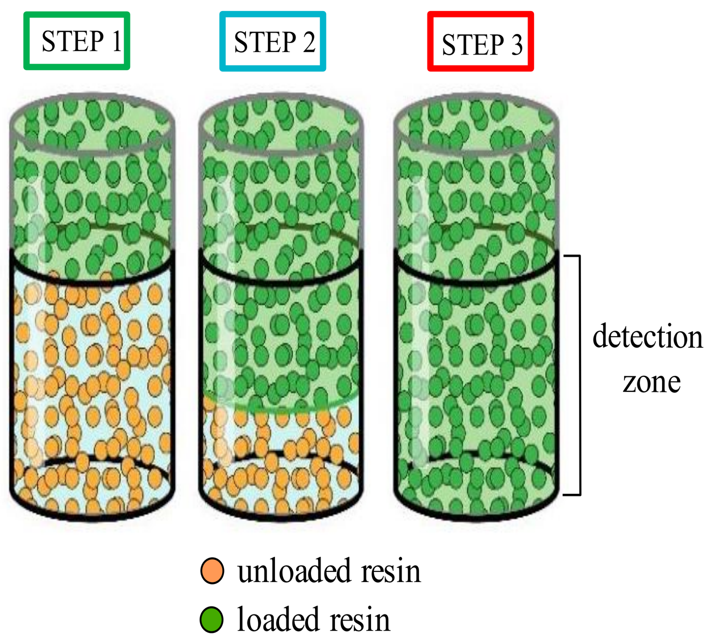
- Resin: 14 g of amberlite IR120, $[Ni^{2+}]$ = 20 mM, flow = 4.3 ml/min, speed of water ≈ 14 mm/min,
- Column (ø = 2 cm) directly inserted in the bore of a low-field NMR device working at 8.33 MHz,
- Height of the resin bed: 5cm, height of the detected zone: 3cm => signal from a part of the bed,

=> choice to study the bottom zone => follow-up of the complete saturation of the column,

- T_2 relaxation curves measured with a CPMG sequence (16000 echoes, TE = 0.3 ms).

5. Results and interpretation

- T_2 relaxation curves clearly multiexponential => biexponential fitting
- Three steps observed for the evolution of the slowly relaxing fraction:



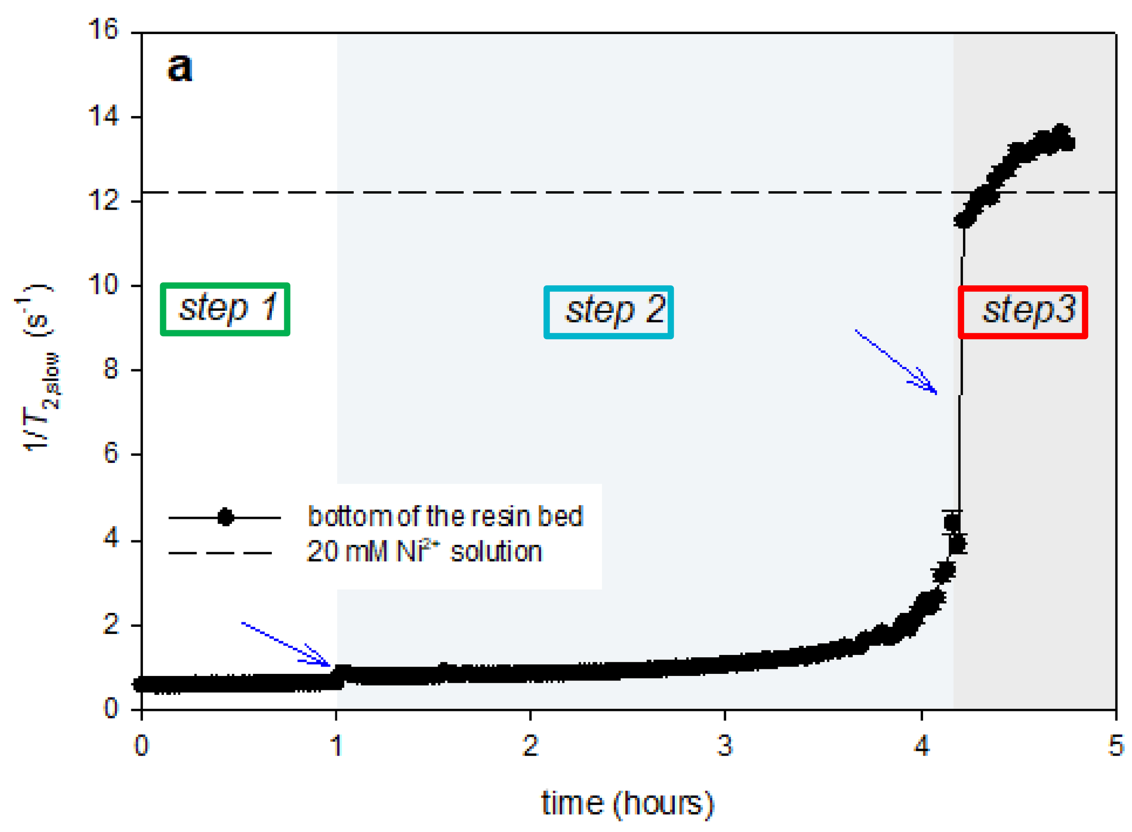


Figure 2: Evolution with time of $1/T_2$ of the slowly relaxing fraction for the bottom of the resin bed

-step 1: the Ni^{2+} solution hasn't reached the studied zone yet,

- ❑ slow fraction = pure water in interporosity (between the beads)
- ❑ fast fraction = water in the intraporosity (in the resin beads)

-step 2: the Ni^{2+} solution has reached the zone => loading of the resin,

- ❑ slow fraction = pure water + water with small Ni^{2+} concentration in the interporosity
- ❑ fast fraction = concentrated Ni^{2+} solution (interporosity) + water in intraporosity (⚠ missed fraction)

-step 3: all resin beads saturated with Ni^{2+}, above and in the studied zone,

- ❑ slow fraction = flowing 20 mM Ni^{2+} solution (in the interporosity) => T_2 ~ 70 ms
- ❑ fast fraction = water in the intraporosity of the Ni^{2+}-loaded resin beads => ultrafast T_2 ~ 1ms

The T_2 distribution obtained by Inverse Laplace Transform confirms the 3 separate steps.

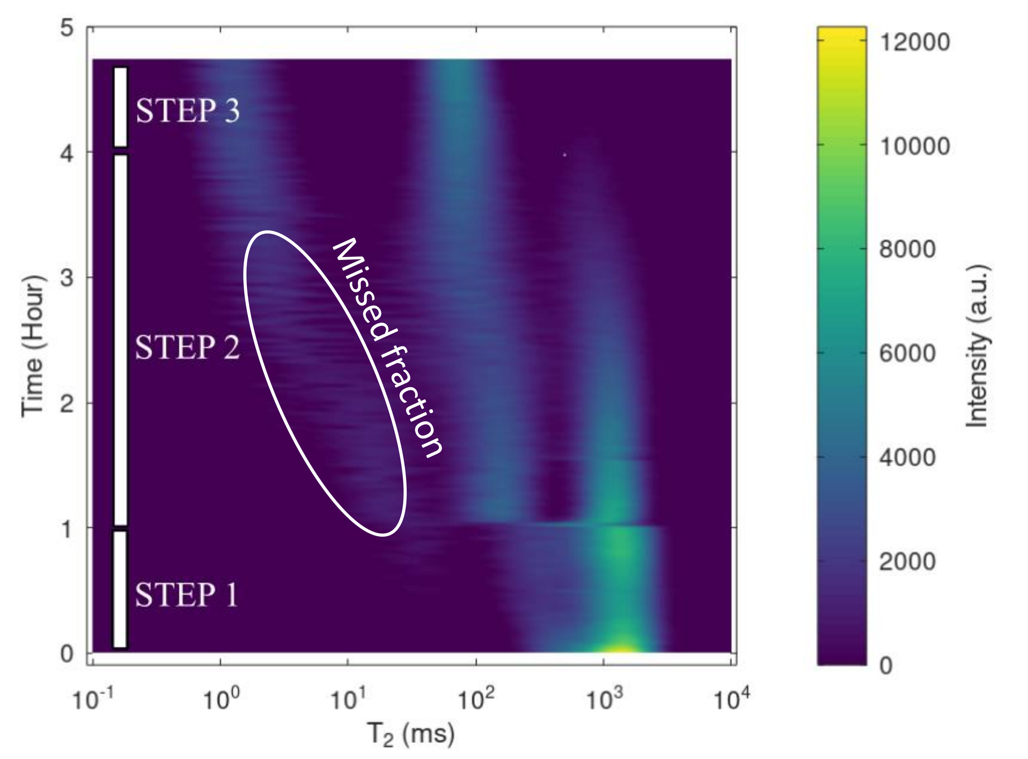


Figure 3: Evolution with time of the T_2 distribution for the bottom of the resin bed

Transition between steps 1 and 2 (blue arrow)
= arrival of the 20mM Ni^{2+} solution in the zone,
Transition between steps 2 and 3 (blue arrow)
= saturation of the entire resin bed with Ni^{2+},
=> Detection by NMR of the saturation of the bed is possible
=> Good agreement with the evolution of $[Ni^{2+}]$ in the effluent measured by ICP-AES.

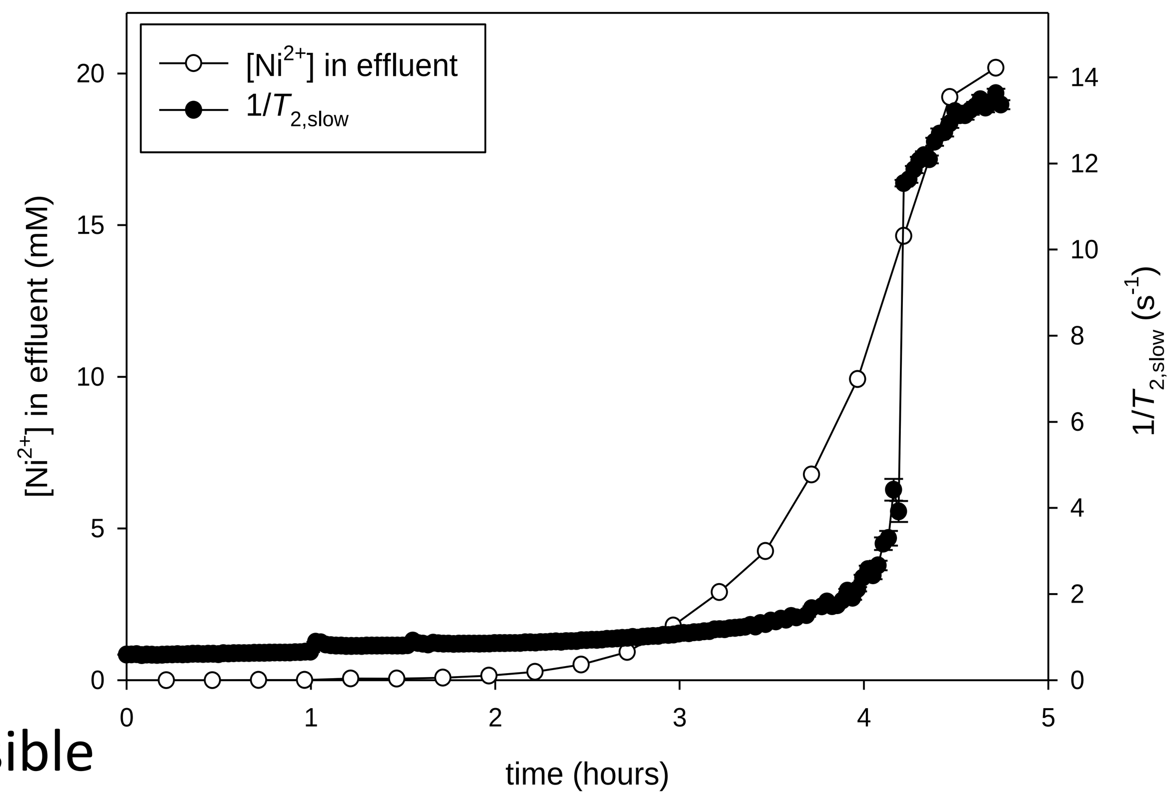


Figure 4: Comparison of the relaxation results with the evolution of $[Ni^{2+}]$ in the effluent measured by ICP-AES

6. Perspectives

- Same experiment with lower paramagnetic ion concentration (<< 1 mM),

=> closer to real life conditions but the fitting and interpretation must be adapted,

=> Follow-up of the water relaxation in the intraporosity, with very short T_2 ?

- Study of other adsorbents and other paramagnetic ions (Cu^{2+} already done).

References

1. Gossuin et al, Journal of Water Process Engineering 2020
2. Marchesi et al, Dalton Trans. 2022
3. Bernardi et al, Int. J. Environ. Sci. Technol. 2024

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